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IR Investigation of $Fe(CO)_5$ Adducts at the Surface of Silicalite, ZSM-5, Zeolite Y, and γ-Al_2O_3

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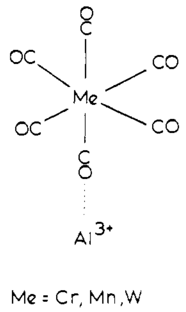
The primary product of the room-temperature interaction of $Fe(CO)_5$ with Lewis and Brønsted acid centers at the surfaces of ZSM-5, H-Y, and γ-Al_2O_3 is in all cases represented by O-bonded adducts. On the basis of a complete vibrational assignment of the IR spectrum of the surface adducts, it is concluded that $Fe(CO)_5$ oxygen bonded to Lewis acid centers has approximate C_{3v} symmetry. The frequencies of the O-bonded carbonyl are lowered by about 150–200 cm^{-1} ($Al^{3+}{}_{tet}$) and 100–150 cm^{-1} ($Al^{3+}{}_{oct}$) with respect to the unperturbed carbonyl molecule, while the other modes are raised by 40–50 and 25–40 cm^{-1}, respectively. In $Fe(CO)_5$ oxygen bonded (or hydrogen bonded) to Brønsted sites (H-Y zeolite), the perturbed carbonyl frequency is 50 cm^{-1} lower than that of the unperturbed carbonyl.

Introduction

A great deal of work has been done on anchoring of the metal carbonyls on various supports for the preparation of catalysts.[1] Depending upon the nature of the support (basic or acidic) and its hydroxylation state, the anchoring process can follow different routes. In fact as the surface of the ionic or partially ionic oxides contain both coordinatively unsaturated cations (Lewis centers) and anions (oxygen, hydroxyl, or both), the basic chemistry can be very complex. For instance, on surfaces dominated by the Lewis acid sites, the coordination of metal cluster carbonyls occurs via oxygen bonding[2] of the bridging CO. Similarly, well-defined mononuclear O-bonded adducts (I) are found upon interaction of group VI mononuclear metal carbonyls with fully dehydroxylated γ-Al_2O_3[3,4] (where the Lewis acidity is the prevailing chemical property).



I

It is most noticeable that once the state of the surface is sufficiently well-defined, the IR spectra of the surface O-bonded adducts are so well-defined that they can be completely compared with those of the homogeneous analogues prepared under homogeneous conditions by interaction of the metal carbonyls with soluble Lewis acids (i.e. $AlCl_3$ and/or $AlBr_3$).[5]

In homogeneous conditions the interaction of metal carbonyls with protons (Brønsted acids) had also been observed.[5,6] There are numerous reports confirming such an interaction on surfaces. For instance Bein et al.[7] have observed that adsorption of $Fe(CO)_5$ in H-Y zeolite causes a distinct perturbation of the acidic OH groups (Brønsted acids): this fact has been interpreted in terms of hydrogen-bond formation between the oxygen of the carbonyl group and the proton (oxygen bonding to proton). On this basis we can suggest that oxygen bonding *is always* the primary step during the interaction of metal carbonyls, both mononuclear and polynuclear, with solid surfaces having acidic (Lewis and Brønsted) character. In order to prove the general validity of the this hypothesis, in this paper we report and discuss the IR spectra of $Fe(CO)_5$ adsorbed on the following materials: silicalite (highly dehydroxylated; no Lewis acidity); ZSM-5 (highly dehydroxylated; Lewis acidity only); H-Y (extra low sodium and NH_4^+, dehydroxylated at 573 K; Brønsted acidity only); H-Y (partially dehydroxylated at 723 K; Brønsted and Lewis acidity); H-Y (nearly totally dehydroxylated at 1073 K; Lewis acidity only); γ-Al_2O_3 (dehydroxylated at 973 K; Lewis acidity only).

The IR spectra of $Fe(CO)_5$ adsorbed on silicalite are reported in this paper for sake of reference. In fact the surface properties of this solid can be considered as a prototype of the adsorbing properties of the covalent and siliceous (Al^{3+}-free) parts of ZSM-5; in fact silicalite is a totally siliceous zeolite with the same structure as ZSM-5.

Experimental Section

The dehydroxylated form (suitable for IR measurements) of ZSM-5 has been prepared by heating under vacuum (10^{-5} Torr) for 3 h at 973 K a pellet of HZSM-5 (from Montedipe; Si/Al = 28). After this thermal treatment the intensity of the OH modes (in the 3750–3500-cm^{-1} range) is almost nil, so ensuring that Brønsted acidity is negligible.

Identical thermal treatment has been made on the silicalite pellet (also in this case the IR bands of the residual OH groups were hardly detectable).

H-Y zeolite has been obtained from NH_4^+-exchanged Y-zeolite (Linde, low sodium LZ-Y82), with the following typical composition: SiO_2, 72.2 wt %; Al_2O_3, 22.8 wt %; Na_2O, 0.2 wt %; $(NH_4)_2O$, 4.4 wt %; SiO_2/Al_2O_3, molar ratio 5.38; Na_2O/Al_2O_3, molar ratio 0.01.

The decomposition of the sample to give the protonated form (H-Y) has been made by following standard procedures.[8]

(H-Y) samples thermally treated in vacuo at 573 K predominantly contain Brønsted acidity,[8] while the samples outgassed in vacuo at 723 K contain both Brønsted and Lewis acidity.[8,9]

A nearly complete dehydroxylation and a maximum of Lewis acidity can be achieved at 1073 K under vacuo for 3 h. At this temperature a little skeletal degradation of the zeolite has been reported to occur. However, this is not influential for the purposes of this investigation.

Finally fully dehydroxylated γ-Al_2O_3 (Degussa, aluminum oxide C) has been obtained by thermal treatment under vacuo at 973 K for 3 h. Inspection of the OH-stretching region reveals that, after this thermal treatment, the intensity of the OH modes in the 3750–3550-cm^{-1} range is negligible. These samples are also characterized by the maximum surface Lewis acidity. The morphology of this γ-Al_2O_3 particles has been recently examined by Reller and Cocke:[10] the microparticles are perfect single crystals of hexagonal shape (with a diameter of 10–20 nm and thickness below 5 nm).

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The $Fe(CO)_5$ (Strem) has been dosed from the gas phase after double distillation.

The IR spectra have been made with a Perkin-Elmer 580B instrument equipped with a data station. The spectra reported in the figures are blank subtracted.

Results and Discussion

(1) Perturbation Caused by Oxygen Bonding (to Surface Lewis and Brønsted Sites) on the IR Spectrum of $Fe(CO)_5$: A General Introduction. (a) Lewis Sites.

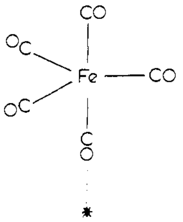
In the gas phase, $Fe(CO)_5$ is a trigonal bipyramid with D_{3h} symmetry. The CO stretching representation is

$$\Gamma_{CO} = 2A_1' + A_2'' + E'$$

and only the A_2'' and E' (doubly degenerate) modes are IR active [actually two IR bands at 2012 (E') and 2034 (A_2'') cm^{-1} are observed].[11]

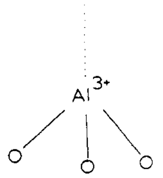
In solution in a nonpolar solvent, $Fe(CO)_5$ behaves very similarly. The only small differences are that (a) the E' mode is shifted to lower frequencies (2000 cm^{-1}) and (b) the A_2'' mode is shifted downward to 2022 cm^{-1}. Solid and liquid $Fe(CO)_5$ give a spectrum essentially similar to that of the solution, the main difference being represented by two very weak components at 2115 and 2033 cm^{-1}, associated with the Raman-active modes [$\nu_1(A_1')$ and $\nu_2(A_1')$, respectively].[11] The previously discussed spectra of $Fe(CO)_5$ in the condensed phase will be taken as a reference for $Fe(CO)_5$ physically adsorbed on the surface or condensed into channels (for instance for $Fe(CO)_5$ on silicalite or on Al-free part of ZSM-5 and zeolite-Y surfaces).

Anchoring of $Fe(CO)_5$ to Lewis acid surface sites via oxygen bonding gives adducts of approximate C_{3v} symmetry (II); the asterisk indicates a coordinatively unsaturated Lewis center.



II

Adducts with tetrahedral $Al^{3+}{}_{cus}$ (type a) should be the dominant ones on the dehydroxylated forms of ZSM-5 and Y-zeolites (because the aluminum ions, being substitutive of silicon in the tetrahedral units of the zeolites, are retaining the tetrahedral structure). Of course exposed Al^{3+} ions in the external surface or in the cages and channels can have one coordinative unsaturation point (III) and consequently they can act as efficient Lewis acceptors. Another type of Lewis acceptor site could be represented by coordinatively unsaturated (positively charged) silicon atoms, formed during the last steps of the dehydration stage.[12] However, as their structural character is similar to that of the $Al^{3+}{}_{cus}$, we shall consider them all together.



III

Type a adducts should also be present on γ-Al_2O_3 surfaces. In fact, as γ-Al_2O_3 has a defective spinel type structure,[13] the Al^{3+} ions of the bulk occupy both tetrahedral and octahedral holes: consequently some tetrahedral ions are necessarily emerging on the surfaces (although not necessarily in the same concentration as in the bulk). Adducts with octahedral $Al^{3+}{}_{cus}$ ions (type b structure) should be absent on dehydroxylated zeolites but should be present on γ-Al_2O_3 surface. As the Lewis acidity of the $Al^{3+}{}_{tet}$ ions is expected to be larger than that of the $Al^{3+}{}_{oct}$ ones,[14,15] a-type adducts are more stable than the b-type adducts. An important difference between dehydroxylated γ-Al_2O_3 and dehydroxylated ZSM-5 and H-Y zeolites lies in the fact that while on zeolites the Lewis acids ($Al^{3+}{}_{tet}$) are isolated ones with respect to the others (particularly in ZSM-5, because the Si/Al ratio is very large), on γ-Al_2O_3 they are not isolated. For this reason the surface properties of the γ-Al_2O_3 surface cannot be simply considered as the mere sum of the properties of individual $Al^{3+}{}_{tet}$ and $Al^{3+}{}_{oct}$ sites. Consequently, in this case, it is more appropriate to speak in more general terms of Lewis sites whose acidity is predominantly determined by $Al^{3+}{}_{tet}$ and $Al^{3+}{}_{oct}$ ions respectively.

Another additional source of difficulties with γ-Al_2O_3 lies in the fact that the molecules of $Fe(CO)_5$ adsorbed on nonisolated Lewis sites necessarily interact both *through space* (steric and dipole–dipole dynamic effect) and *through solid* (chemical effects).[4] These type of effects, which are typical of the surface chemistry and physics, can all be collected together under the wide concept of adsorbate–adsorbate interactions. As far as the most important "chemical" (through solid) effects are concerned, the formation of a and b type adducts through oxygen bonding of CO terminal groups involves σ-donation to Lewis centers. The donated charge is dissipated through the solid, and the electron density at the adjacent and more distant Al^{3+} sites increases (the effect is thought to die away in a few lattice spacings). Incoming $Fe(CO)_5$ molecules find surface sites with decreasing σ-acceptor capacity: hence the strength of oxygen bonding is expected to decrease gradually with increasing θ (as already observed for the interaction of $Mo(CO)_6$ with γ-Al_2O_3).[4]

Of course, partially hydrated surfaces are even more complicated, because, besides Lewis acidity, different types of OH groups (characterized by a broad spectrum of Brønsted acidity) must be considered. Moreover, a reaction between OH groups and adsorbed carbonyl, accompanied by release of H_2, cannot be excluded.[16] For the sake of simplicity, in this paper only totally dehydroxylated Al_2O_3 surfaces will be taken into consideration.

The Γ_{CO} of the oxygen-bonded adducts a and b (local symmetry C_{3v}) is

$$\Gamma_{CO} = 3A_1 + E$$

By analogy with the known homogeneous O-bonded analogues[5] and with the heterogeneous ones formed by interaction of metal VI carbonyls on γ-Al_2O_3,[4] oxygen bonding should have the following effects: (a) the stretching band of the O-bonded CO $(A_1)_3$ is expected to shift downward [$\Delta\bar{\nu} \approx -(150\text{–}200)$ cm^{-1} for the a-type complex and $\Delta\bar{\nu} \approx -(100\text{–}150)$ cm^{-1} for the b-type complex]; (b) the stretching modes of the remaining $Fe(CO)_4$ moiety (a total of three IR bands: $2A_1 + E$) are expected to move upward with respect to the modes of the unperturbed (D_{3h}) carbonyl. On the basis of the results shown in ref 4, the upward shift of two A_1 modes and of the degenerate E mode should be approximately $\Delta\bar{\nu} = +(40\text{–}50)$ cm^{-1} for a-type adducts and $\Delta\bar{\nu} = +(25\text{–}40)$ cm^{-1} for the b-type adducts.

The total increase of the frequency of the four $3A_1 + E$ modes [$\Delta\bar{\nu}_{tet} = +(160\text{–}200)$ cm^{-1} for a-type and $\Delta\bar{\nu}_{oct} = +(100\text{–}160)$ cm^{-1} for b-type adducts] roughly counterbalances the downward shift of the O-bonded CO, as found in homogeneous Lewis O-bonded carbonyls[5] and on γ-Al_2O_3.[4]

On the basis of the previous considerations, the approximate IR pattern shown in Figure 1 is schematized for the a-type and b-type adducts. The Figure 1 pattern is based on the perturbed bipyramidal $Fe(CO)_5$ model. Another, less likely, structure could be the axially coordinated square pyramid, which cannot "a priori"

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Table I

		IR, cm^{-1}				
		ZSM-5 (973 K)	H-Y (573 K)	H-Y (723 K)	H-Y (973 K)	γ-Al_2O_3 (973 K)
adduct a (tet)	$(A_1)_1$	2134		2135	2135	2150–2135
	$(A_1)_2$	2065		2066	2066	2085–2080
	(E)	2048		2050	2050 (sh)	2060–2055
	$(A_1)_3$[a]	1840	1850	1850	1840	1840–1800
adduct b (oct)	$(A_1)_1$					2130–2125
	$(A_1)_2$					2180 }
	(E)					2150 } *b*
	$(A_1)_3$[a]					1845–1910
adduct c	$(A_1)_1$		2118	2118		
	$(A_1)_2$		2038	~2038 }		
	(E)		2015	~2015 } *b*		
	$(A_1)_3$[a]		1950	1950	1945 (sh)	

[a] O-bonded CO. [b] Complex unresolved adsorption superimposed on adduct a modes.

be discarbed because of the fluxionality of $Fe(CO)_5$. However, as the spectroscopic features of both the starting and the anchored complexes are very similar, we shall hereafter refer to the trigonal bipyramid only.

In Figure 1 the IR peaks of the various types of O-bonded adducts are located at frequencies that are assumed to be independent of the coverage changes. For γ-Al_2O_3 this is a crude approximation. In fact, due to the strong (through solid) chemical effects, the Lewis acidity of the nonindependent sites decreases with an increase in θ. As a consequence the stretching frequency of the CO groups (and particularly that of the O-bonded ones) will gradually change with θ (as already observed).[4]

(b) Brønsted Sites. Many cases are known under both homogeneous[17,18] and heterogeneous conditions[5,7,19,20] of hydrogen bonding. Consequently the formation of $(CO)_4Fe$–$CO\cdots H^+$ structures: (adduct c) must be considered. The spectroscopic effect of hydrogen bonding is to decrease the carbonyl frequency by about 50 cm^{-1}.[5,17] At the same time the vibrations of the $-Fe(CO)_4$ moiety in adduct c should be very slightly affected, and fall at nearly the same frequency of the physically adsorbed species.

Of course, the vibrations of the acidic OH groups should be simultaneously affected by the formation of the hydrogen bond. For instance a decrease of intensity of the 3645-cm^{-1} band (acidic OH sites) of H-Y zeolite upon dosing with $Fe(CO)_5$ has been explained in this way by Bein et al.[7]

(2) IR Spectrum of $Fe(CO)_5$ Adsorbed on Silicalite and ZSM-5 in the Highly Dehydroxylated Form. Silicalite and ZSM-5 are both zeolites of the pentasil family.[21] The diameter of the channels (d = 0.53 nm) is too small to allow the penetration of the big carbonylic molecules (effective diameter 0.7 nm) at room temperature.[22] Consequently $Fe(CO)_5$ is adsorbed only on the external faces of the zeolite crystallites. The IR spectrum of $Fe(CO)_5$ adsorbed on highly dehydroxylated (973 K) silicalite (Figure 2a) is similar to that expected for a physically adsorbed species. In fact only the A_2'' and E modes appear with strong intensity and with frequencies intermediate between those of the gas phase and the condensed phase.[11] The $\nu_1(A_1')$ mode at 2115 cm^{-1} is also observed with very weak intensity (as expected for a mode that is IR inactive in the gas phase). The small band at ~2080 cm^{-1} is a combination mode as found in both the gaseous and liquid phases.[11]

The IR spectrum of $Fe(CO)_5$ adsorbed on highly dehydroxylated (973 K) ZSM-5 is characterized by several additional bands (2134, 2065, 2048, and 1840 cm^{-1}) (Figure 2b). Comparison of the spectra of $Fe(CO)_5$ adsorbed on silicalite and on ZSM-5 (Figure 2c) allows us to conclude that (a) the peaks at 2027 and 2017 cm^{-1} belong to $Fe(CO)_5$ physically adsorbed on the siliceous (Al-free) parts of the surface (because they are identical with those found for $Fe(CO)_5$ adsorbed on silicalite) and (b) the four additional peaks at 2134 2065, 2048, and 1840 cm^{-1} belong to $Fe(CO)_5$ adsorbed onto exposed $Al^{3+}{}_{cus}$ ($Si^{4+}{}_{cus}$) ions (cus = coordinatively unsaturated).

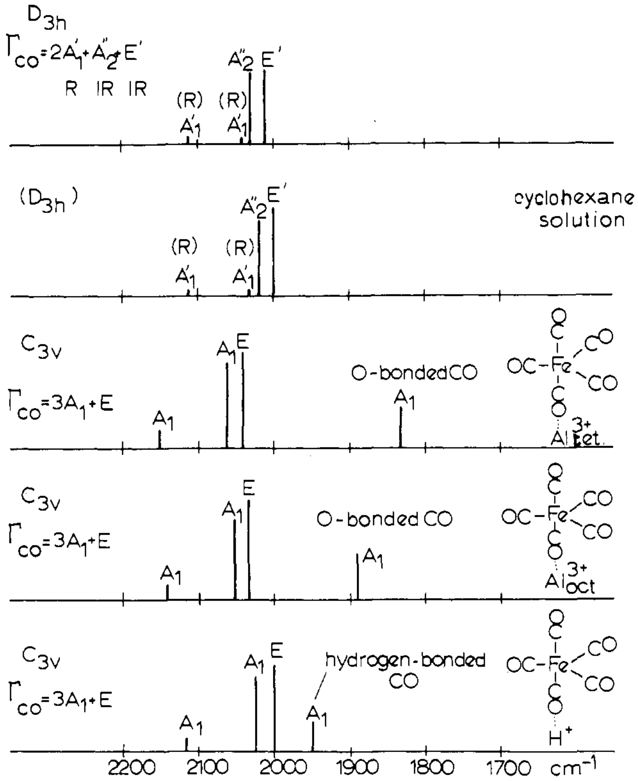

Figure 1. Schematic representation of the vibrational modes of $Fe(CO)_5$ adducts formed upon interaction with different types of Lewis and Brønsted sites. Only Al sites are considered for sake of simplicity.

On the basis of Figure 1, the assignment is straightforward (Table I): *the four bands belong to the a-type O-bond adducts.* With respect to the schematic representation of Figure 1, there is however a small but significant difference: in fact the A′ mode at 2065 cm^{-1} is found to be stronger than the E mode (while on the basis of the simple considerations of the previous paragraph the opposite is expected). The different spectra illustrated in Figure 2b, have been obtained during a desorption experiment at the IR beam temperature (~323 K) by gradually reducing the pressure of $Fe(CO)_5$ in equilibrium with the sample. The large intensity decrease obtained by simply decreasing the $Fe(CO)_5$ pressure demonstrates the reversible nature of the $Fe(CO)_5$ adsorption on the external surface of ZSM-5. This experimental observation must be kept in mind, because the behavior of $Fe(CO)_5$ on dehydroxylated H-Y is quite different (even if the IR spectrum

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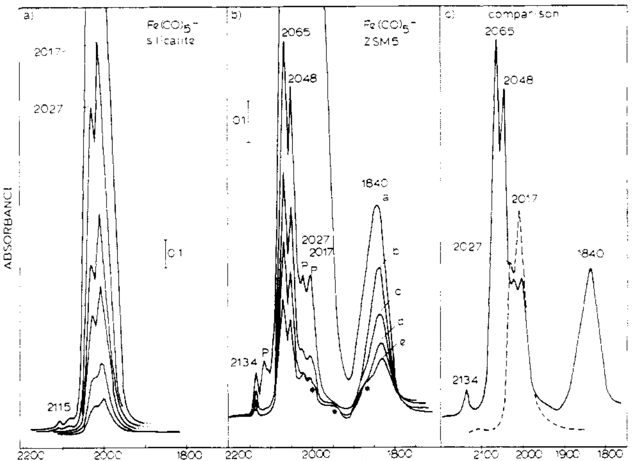


Figure 2. (a) $Fe(CO)_5$ adsorbed on silicalite degassed at 973 K. Different spectra correspond to increasing coverages of $Fe(CO)_5$ on silicalite (spectra a, p ($Fe(CO)_5$) = 20 Torr). The spectra are highly reversible upon decreasing the pressure. (b) Adsorption–desorption spectra of $Fe(CO)_5$ on ZSM-5 degassed at 973 K. Spectrum a is obtained upon dosing 20 Torr of $Fe(CO)_5$ on ZSM-5. Spectra b–e are obtained upon evacuation of the compound obtained under the conditions in part a for 90 s, 6 min, 25 min, and 50 min, respectively. (c) Comparison of spectra of comparable intensities of $Fe(CO)_5$ on silicalite (broken line) and ZSM-5 (full line), that are shown in parts a and b.

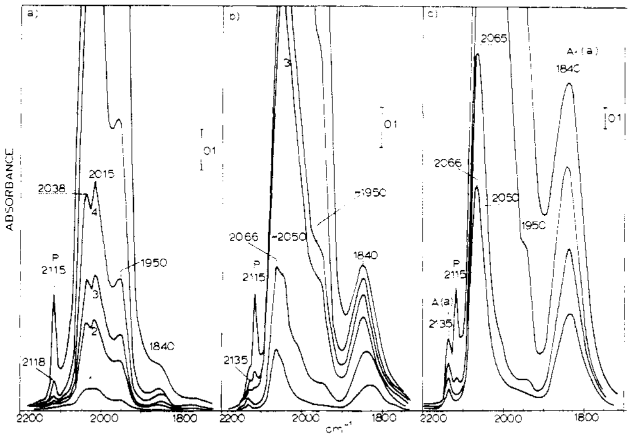


Figure 3. (a) Spectra of $Fe(CO)_5$ on H-Y zeolite degassed at 573 K for 3 h. Different curves correspond to increasing coverages of $Fe(CO)_5$. The spectrum with the highest intensity is obtained upon contacting 20 Torr of $Fe(CO)_5$ with ZSM-5. The spectra are highly reversible. (b) Spectra of $Fe(CO)_5$ on H-Y outgassed for 3 h at 723 K. Different spectra correspond to increasing coverages. Spectrum of maximum intensity correspond to p = 20 Torr of $Fe(CO)_5$. These spectra are only slightly affected by pumping at room temperature. Evacuation at room temperature slowly eliminates only the physically adsorbed $Fe(CO)_5$ (peak at 2115 cm^{-1} and absorption at 2000 cm^{-1}). (c) Spectra of $Fe(CO)_5$ on H-Y zeolite degassed at 1073 K for 3 h. The spectrum with maximum intensity is obtained with 10 Torr of $Fe(CO)_5$, and the other spectra are obtained by evacuating the compound obtained under the conditions used for this spectrum for 40, 60, and 80 min, respectively.

of adsorbed $Fe(CO)_5$ is basically identical).

The peaks indicated with asterisks are not so clearly visible when the adsorption experiment is carried out; consequently, they must be assigned to decarbonylation products. Due to the limited scope of this investigation we shall not discuss this problem in detail: it will represent the main subject of a study of the decarbonylation of mononuclear carbonyls on acidic surfaces.

(3) IR Spectra of $Fe(CO)_5$ Adsorbed on H-Y at Different Dehydration Stages. In Figure 3a–c the IR spectra of increasing doses of $Fe(CO)_5$ adsorbed on H-Y (excess NH_4^+Y) thermally treated in vacuo at 573, 723, and 1073 K are reported.

If only the spectra corresponding to pore filling, far from the saturation, are considered, we can conclude that they are the superimposition of two sets of four bands.

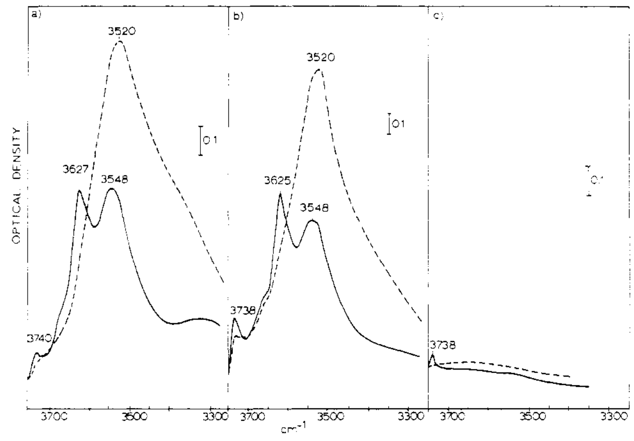


Figure 4. Spectra a–c showing the consumption of hydroxyl groups upon dosing $Fe(CO)_5$ on H-Y zeolite outgassed at 573, 723, and 1073 K, respectively.

The first set (peaks at 2118, 2038, 2015, and 1950 cm^{-1}), which is dominant for the protonated form (Figure 3a) and nearly absent for the dehydroxylated one (Figure 3c), is assigned to hydrogen-bonded species (as hypothesized in Figure 1). In fact *it is characterized by a new frequency at 1950 cm^{-1} clearly associated with the stretching mode of the hydrogen-bonded CO.*

The second set (frequencies at 2135, 2066, 2050, and 1840 cm^{-1}), which is dominant for the hihgly dehydroxylated form (Figure 3c) and nearly absent for the protonated one, *is readily assigned (by comparison with the spectrum of $Fe(CO)_5$ on ZSM-5) to a-type adducts.* Of course these adducts are now primarily located in the cages of the zeolites.

H-Y samples treated at intermediate temperatures (723 K) show the simultaneous presence of both species with comparable intensity (Figure 3b).

Spectra corresponding to saturation values approaching 100% are very intense due to the growth of the contribution of the liquid-like species, whose only clearly observable band is the (Raman-active) A_1 mode at 2115 cm^{-1}.

The formation of the hydrogen-bonded species (1950 cm^{-1}) on both the 573 and 723 K treated samples is confirmed by the spectra shown in Figure 4a–c; which illustrates the effect of $Fe(CO)_5$ on the OH stretching modes.

In fact the peak at 3625 cm^{-1} corresponding to the stretching mode of the OH groups in the supercages[7] are totally consumed (upon dosing with $Fe(CO)_5$) with subsequent formation of a strong peak at 3520 cm^{-1} (hydrogen-bonded species). In agreement with the previous assignment, the formation of hydrogen-bonded species gradually declines with an increase of the thermal pretreatment and is practically absent for fully dehydroxylated samples. Despite thus, in Figure 3c we observe a residual shoulder at ~1950 cm^{-1}, indicating that the interaction of $Fe(CO)_5$ with positive centers is still present. As Na^+ centers (which are permanent impurities) can act as weak Lewis acceptors toward $Fe(CO)_5$, as found under homogeneous conditions,[5] the residual presence of the 1950-cm^{-1} band can be rationalized. In this respect we may recall the published IR spectra of $Fe(CO)_5$ on Na-Y and H-Y zeolites, which are remarkably similar, and both show the presence of IR peaks at ~1950 cm^{-1}.[22]

A remarkable difference between the $Fe(CO)_5$/(ZSM-5 or silicalite) and the $Fe(CO)_5$/H-Y (1073 K) systems is represented by the larger reversibility (upon beam temperature outgassing) of the $Fe(CO)_5$ species adsorbed on ZSM-5 and silicalite (see captions of Figures 2 and 3). This point, already observed and discussed by Bein et al.,[7,22] is due to the fact that in the $Fe(CO)_5$/H-Y system the carbonyl is located in the supercages while in the $Fe(CO)_5$/(ZSM-5 or silicalite) system the carbonyl is adsorbed on the external surface of the zeolite.

(4) IR Spectra of $Fe(CO)_5$ Adsorbed on Fully Dehydroxylated Al_2O_3. Unlike ZSM-5 and Y-zeolites, the Al^{3+} ions of γ-Al_2O_3 occupy both tetrahedral and octahedral positions [$Al^{3+}_{tet}/Al^{3+}_{oct}$ = 8/13 (1/3)]. A a consequence, on the external surface of the

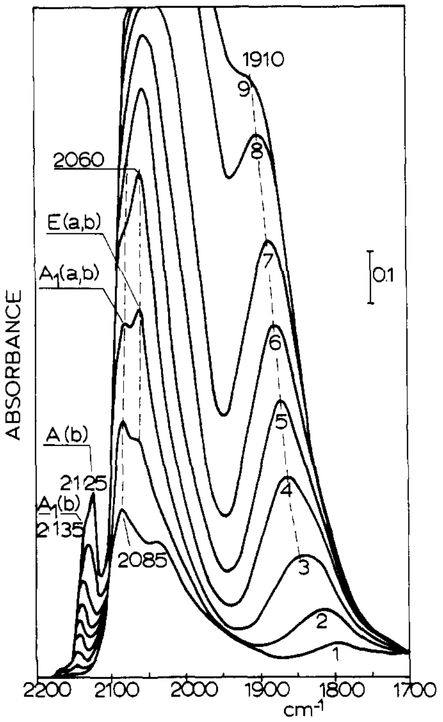
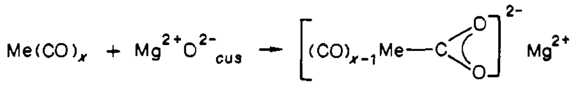


Figure 5. Spectra of $Fe(CO)_5$ on γ-Al_2O_3 degassed at 973 K. Spectrum 9 is obtained upon dosing 15 Torr of $Fe(CO)_5$ on γ-Al_2O_3. The remaining spectra 8–1 are obtained by evacuating the compound obtained under the conditions used for spectrum 9 for 10 s, 40 s, 100 s, 3 min, 8 min, 20 min, 30 min, and 60 min, respectively.

γ-Al_2O_3 microcrystals, sites containing both types of aluminum ions are emerging in variable proportions, depending on the index of the crystallographic surface planes and the surface reconstruction.

Another difference between zeolite and γ-Al_2O_3 is represented by the high ionicity of the γ-Al_2O_3. Consequently we have to consider the possibility that some of the oxygen ions emerging at the surface can manifest Lewis basicity.

$Fe(CO)_5$ interacting with such a complex surface can give (1) with Lewis acid centers a-type and b-type adducts and (2) with Lewis basic centers carbenoid-type adducts similar to those formed upon interaction of metal carbonyls with solid bases like MgO,[23] following the reaction



$$Me(CO)_x + Mg^{2+}O^{2-}_{cus} \rightarrow \left[(CO)_{x-1}Me{-}C\begin{matrix}O\\ \\O\end{matrix}\right]^{2-} Mg^{2+}$$

The second type of surface compound shows two characteristic IR bands in the 1526–1482- and 1063–1050-cm^{-1} intervals. As these bands are not observed in γ-Al_2O_3, we conclude that *Lewis basicity is playing a minor role* in determining the surface properties of the γ-Al_2O_3/metal carbonyl system. Consequently, we shall concentrate only on the Lewis acidity. As two main types of nonisolated Al^{3+} ions are present on γ-Al_2O_3, we expect two types of adducts chemically interacting through solid (i.e., those corresponding to the sites with Lewis acidity predominantly determined by $Al^{3+}{}_{tet}$ and $Al^{3+}{}_{oct}$, respectively).

Inspection of Figure 5 immediately indicates the following.

(1) The complex adsorption moving upward with increasing coverage from 1800 ($\theta \rightarrow 0$) to 1910 cm^{-1} is due to the superimposition of two bands associated with the Fe–CO···Al^{3+} (A_1) vibration of two O-bonded *interacting* carbonyls (with essentially a-type and b-type characters).

The gradual increase in frequency with increasing coverage is due to the progressive decrease of the Lewis acid strength brought about by solid chemical interactions.[4,15] The composite nature of the main peak is indicated by the shoulder in the low-frequency side, which becomes a definite band at the lowest coverages.

It is most interesting to note that at the lowest θ (i.e., when the coverage is sufficiently low that the $Fe(CO)_5$ molecules are not interacting) the frequency of the O-bonded CO is very near to that observed on ZSM-5 and dehydroxylated H-Y (Table I).

(2) The highest frequency absorption (2145–2125 cm^{-1}) is clearly the superimposition of two bands, one dominant at high θ, the second emerging gradually when the equilibrium pressure is decreased. This complex absorption is assigned to the A_1 mode of the $Fe(CO)_4$ moiety of two different surface adducts (Table I) associated with sites containing $Al^{3+}{}_{tet}$ (a type) and $Al^{3+}{}_{oct}$ (b type) respectively. The gradual downward shift with increasing θ is a consequence of the chemical interaction (see the spectra).

(3) The main absorption in the 2080–2040-cm^{-1} range (where this doublet is clearly seen in spectra 2, 3, and 5 in Figure 5) is composite and it is likely the superimposition of the remaining A_1 and E modes of the two different a and b types of surface adducts (Table I). A gradual frequency shift with θ is also observed here.

At the lowest θ (spectrum 1 shown in Figure 5; desorption experiment at the beam temperature), two very weak features are observed at 2165 and 1720 cm^{-1}. By analogy with the γ-Al_2O_3/group VI metal carbonyls system,[4] they could be assigned to two modes of $Fe(CO)_5$ adsorbed on rare (defective) extremely acidic sites. Following this hypothesis, the 1720- and 2165-cm^{-1} bands are the lowest (A_1: O-bonded) and highest (A_1) modes of this low concentration surface adduct, the other modes being buried by the IR manifestations of the other species. Finally, the 2035-cm^{-1} shoulder clearly observable only after outgassing at the beam temperature (spectrum 1 in Figure 5) could be due to small iron cluster carbonyls or CO linearly adsorbed on small iron particles.[23] That a small amount of high nuclearity molecular cluster or highly dispersed iron is formed upon outgassing at the beam temperature is demonstrated by successive contact with CO at high pressure. In fact the classical spectrum (although with reduced intensity) of the adsorbed $Fe(CO)_5$ appears quickly again. The $Fe(CO)_5$ presumably derives from the disintegration of iron clusters or Fe particles in the presence of excess CO. Due to the limited scope of this investigation, the problem of the decarbonylation and of the formation of dispersed metal clusters and particles will not be discussed here in detail.

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Registry No. $Fe(CO)_5$, 13463-40-6; Al_2O_3, 1344-28-1; SiO_2, 7631-86-9.

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